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Variable Activity of Reagents with C=C and N=N Bonds in Cycloaddition Reactions

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Abstract—Data on rates and enthalpies of the reactions of quadricyclane (**4**) and diadamantylidene (**5**) with *N*-phenylmaleimide (**1**), 4-phenyl-1,2,4-triazoline-3,5-dione (**2**), and tetracyanoethylene (**3**) are obtained for the first time. Reagent **2** with the N=N reaction center is found to be six orders of magnitude more active than its structural analog **1**. A strong π-acceptor 3 is 370 times more active than reagent **2** in the reaction with a strong π-donor substrate **4** but is less active than reagent 2 in many [4π + 2π], [2π + 2π + 2π], and [2π + 2π] cycloaddition reactions, and, especially, in ene reactions. The possible causes of the strong difference and variable activity of compounds **1**–**3** with C=C and N=N bonds are discussed.

Keywords: reaction rate, enthalpy of reaction, cycloaddition reactions, ene reactions

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INTRODUCTION

There is keen interest in cycloaddition reactions, as they have a broad synthetic potential [1]. Furthermore, intense attention is paid to these reactions, and in particular to the Diels–Alder reaction, because these reactions occur in a quantitative yield and the data on the effect of various factors on their rates and equilibrium are reliable [2]. It has been demonstrated for a wide range of dienes and dienophiles with the C=C reaction centers that the rate of the Diels–Alder reaction ($\log(k_2$, k_2/L mol^{-1} s^{-1})) depends on the ionization potential (IP_D, eV) of a diene, electron affinity energy (E_A, eV) of a dienophile, the balance between the energy of bond rupture and formation ($\Delta H_{r\text{-}n}$, kJ mol^{-1}), and the distance between the reaction centers **1**–**4** (see below) in a diene ($R_{C(1)-C(4)}$, Å) [2]:

$$\log k_2 = -28.81 + \frac{316.3}{IP_D - E_A} - \frac{69.9R_{C(1)-C(4)}}{IP_D - E_A} - 0.054\Delta H_{r-n}.$$

This relationship permits the prediction of the rate of Diels–Alder reactions involving those C=C bonds that have not been studied yet and planning of the experimental conditions. However, the rate of Diels–Alder reactions involving N=N bonds is not described by this equation. Thus, activity of *N*-phenyl maleimide (**1**) with the C=C reaction center in Diels–Alder reactions with different dienes is five to six orders of magnitude lower than that of its structural analog, 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) with the N=N reaction center, although their E_A values are close (~1 eV) [2, 3]. Furthermore, in the Diels–Alder reactions with dienes having weak π-donating properties, the reaction rate of even tetracyanoethylene (**3**), one of the strongest π-acceptors (E_A = 2.88 eV [4]) and the most active dienophiles with the C=C reaction center, is usually lower than that of dienophile **2** [2, 3]. However, dienophile **3** was found to be more active than dienophile **2** in the Diels–Alder reaction with strong π-donating dienes, such as substituted anthracenes (IP_D = 7.0–7.5 eV) [3, 5].

In order to obtain novel data for the reactions involving the C=C and N=N bonds, we studied the kinetics and calorimetric parameters of the reactions of [2π + 2σ + 2σ] cycloaddition of **1**–**3** to reagent **4** and [2π + 2π] cycloaddition to reagent **5** (Fig. 1). The findings were compared to the results for the [2π + 2π + 2π] and [4π + 2π] cycloaddition reactions and ene reactions between reagents **1**–**3** and substrates **6**–**11** (Fig. 2).

EXPERIMENTAL

Quadricyclane was synthesized using the procedure described in [6], dried over sodium, and recondensed at lower pressure (600 Pa). Quadricyclane purity was determined by volumetric titration of the reagent with a bright red tetracyanoethylene solution in toluene, since the reaction between reagents **3** and **4** (hereafter, reaction **3** + **4**) occurs very rapidly and is seven orders of magnitude faster than reaction **3** + **6**. The titration results demonstrate that purity of the reagent **4** is 97 ± 0.5%. Diadamantylidene was synthe-